

Peroxides from Autoxidized Methyl Oleate and Linoleate as Initiators in the Preparation of Butadiene-Styrene Synthetic Rubber*

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Aside from a passing reference to the fact that methyl oleate hydroperoxide gives somewhat more rapid polymerization than cumene hydroperoxide in a dihydroxyacetone redox recipe,² long-chain aliphatic peroxides or hydroperoxides derivable from readily available fatty materials have not been studied. Recent reports from these laboratories (E.R.R.L. and N.R.R.L.) have described the convenient isolation in high yield of peroxide concentrates (peroxide content $\geq 75\%$) from autoxidized methyl oleate¹ and methyl linoleate.³ As part of the program to determine the fundamental properties and possible utility of these peroxides, they have been evaluated and compared with two commercial peroxides for use as initiators in the preparation of butadiene-styrene synthetic rubber.

EXPERIMENTAL

Initiators Used. Methyl oleate peroxide (MOP), peroxide content 83%, was prepared from autoxidized methyl oleate by means of the urea complex precipitation technique.¹ Methyl linoleate peroxide (MLP), 41% solution in hexane, was prepared from autoxidized methyl linoleate by the liquid-liquid extraction technique.³ (The terms methyl oleate peroxide and methyl linoleate peroxide are intended to indicate only that the peroxides were obtained from autoxidized methyl oleate and linoleate, respectively, and not that the original *cis* configuration in the unsaturated

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TABLE I
POLYMERIZATION RECIPES EMPLOYING METHYL OLEATE PEROXIDE (MOP)
(Parts by weight)

Ingredient	Dextrose-free redox at 41°F.	Peroxide-dextrose at 122°F.
Butadiene.....	75	75
Styrene.....	25	25
Sulfole B-8.....	0.23	0.23
Potassium soap of rosin acids ^a	4.6	—
Potassium soap of fatty acids ^a	—	4.3
Potassium chloride.....	0.7	—
Potassium hydroxide.....	^b	—
MOP, CHP, or PMHP.....	0.1–0.3	0.05–0.2
Dextrose.....	—	0.1–0.3
Distilled water.....	180	180
Ferrous sulfate heptahydrate ^c	0.15	—
Tetrapotassium pyrophosphate, ^c anhydrous.....	0.17	—

^a The emulsifiers were charged on the basis of solids present.

^b The amount used was sufficient to adjust the pH of the soap solution to 10.5 ± 0.2 .

^c The activator system was aged for ten minutes at 140°F. in eleven parts of reserved water.

TABLE II
POLYMERIZATION RECIPES EMPLOYING METHYL LINOLEATE PEROXIDE (MLP)
(Parts by weight. Temperature 41°F.)

Ingredient	Low dextrose redox	Dextrose-free redox	Amine
Butadiene.....	71.5	75	71.5
Styrene.....	28.5	25	28.5
Sulfole B-8.....	0.23	0.23	0.16
Potassium soap of rosin acids ^a	4.6	4.6	—
Potassium soap of fatty acids ^a	—	—	4.7
Trisodium phosphate dodecahydrate.....	0.5	—	—
Daxad 11.....	0.1	—	—
Potassium chloride.....	—	0.7	0.4
Potassium hydroxide.....	^b	^c	^c
Triton R-100.....	—	—	0.05
MLP, CHP, or PMHP.....	0.1–0.2	0.1–0.3	0.1–0.3
Diethylenetriamine.....	—	—	0.12
Distilled water.....	180	180	180
Ferrous sulfate heptahydrate.....	0.12 ^d	0.15 ^e	0.003
Tetrapotassium pyrophosphate, an- hydrous.....	0.17 ^d	0.17 ^e	—
Dextrose.....	1.0 ^d	—	—

^a The emulsifiers were charged on the basis of solids present.

^b The amount used was sufficient to adjust the pH of the soap solution to 10.8 ± 0.2 .

^c The amount used was sufficient to adjust the pH of the soap solution to 10.5 ± 0.2 .

^d The activator system was boiled for five minutes in twelve parts of reserved water.

^e The activator system was aged for ten minutes at 140°F. in eleven parts of reserved water.

esters is retained. Furthermore, these peroxides are the mixed peroxides isolated from the autoxidation reaction mixtures and are approximately 80–90% monohydroperoxides and 10–20% peroxides of unknown composition.) Cumene hydroperoxide (CHP) and *p*-menthane hydroperoxide (PMHP) were commercial samples containing 67 and 50% peroxides, respectively, and were obtained from Hercules Powder Company. All peroxides were employed in the polymerization recipe on a 100% purity basis, that is, a sufficient amount of peroxide sample was employed to furnish the desired number of parts of pure peroxide.

Polymerization Recipes. Tables I and II give the recipes employed with MOP and MLP, respectively. Eight-ounce pressure bottles were employed for carrying out the polymerizations.

DISCUSSION

In the dextrose-free recipe at 41°F., MOP and MLP gave higher polymerization rates and conversions than CHP, and they gave as high rates of conversion as PMHP (all comparisons on a molar, but not on a weight, basis). Only about 6×10^{-4} mole of either MOP or MLP is required per one hundred grams of monomers to achieve a rapid and reproducible rate of polymerization. At this initiator content, about 70–85% conversions are obtained in eight hours.

In the peroxide-dextrose recipe at 122°F., at both a low and high dextrose level, MOP appears to be more efficient than either CHP or PMHP, only about half as much MOP (1.5×10^{-4} mole) being employed to achieve the same conversion and polymerization rate. With 1.5×10^{-4} mole of MOP per hundred grams of monomers, about 65–82% conversions are obtained in six hours, the higher conversions being obtained at the higher dextrose level (0.3 part). Increasing the concentration of MOP above 1.5×10^{-4} mole reduced the six hour conversion figure, although a significantly higher initial polymerization rate is observed.

In the dextrose redox recipe at 41°F., MLP gives slightly higher polymerization rates and conversions on a molar basis than CHP or PMHP. About 4.6×10^{-4} mole of MLP is required to obtain 60–65% conversions in about eight hours. On the other hand, in the amine recipe at 41°F., MLP gives slightly lower conversions than either CHP or PMHP.

Although soaps of linoleic acid are well-known retarders for the butadiene-styrene copolymerization,^{4, 5} no such effect was noted in the present investigation with MLP. The failure of MLP to show a retarding effect can be attributed to the fact that it consists mainly of conjugated dienes, and the highly reactive allylic system, typical of unconjugated linoleate, is present only in small amounts.

References

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Synopsis

In the dextrose-free recipe at 41 °F. for the copolymerization of butadiene and styrene, using 6×10^{-4} mole of initiator per one hundred grams of monomers, methyl oleate peroxide (MOP) and methyl linoleate peroxide (MLP) gave higher polymerization rates and conversions than cumene hydroperoxide (CHP), and they gave as high rates of conversion as *p*-menthane hydroperoxide (PMHP). In the peroxide-dextrose recipe at 122 °F., at both low and high dextrose levels, only about one-half as much MOP (1.5×10^{-4} mole) as CHP or PMHP was employed on a molar basis to achieve the same conversion and polymerization rate. In the low dextrose-redox recipe at 41 °F., using 6×10^{-4} mole of initiator per one hundred grams of monomers, MLP gave slightly higher conversions than CHP or PMHP, but in the amine recipe at 41 °F., MLP gave lower conversions.

Résumé

La copolymérisation de butadiène et de styrène a été effectuée en utilisant le récipé sans glucose à 41 °F en présence de 6×10^{-4} de mole d'initiateur par cent grammes de monomères; le peroxyde d'oléate de méthyle (MOP) et le peroxyde de linoléate de méthyle (MLP) permettent d'obtenir des vitesses et des rendements plus élevés que l'hydroperoxyde de cymène (CHP); ils donnent des vitesses aussi élevées que l'hydroperoxyde de *p*-menthane (PMHP). En présence de dextrose, et à 122 °F, aussi bien à faible teneur en dextrose qu'à teneur élevée, on a utilisé seulement la moitié de peroxyde d'oléate de méthyle (1.5×10^{-4} mole) par rapport au CHP ou PMHP; elle permet néanmoins d'obtenir le même degré de conversion et la même vitesse de polymérisation. Avec les récipés redox contenant peu de glucose et utilisant à 41 °F 6×10^{-4} mole d'initiateur par cent grammes de monomères, le MLP fournit des conversions légèrement plus élevées que le CHP ou le PMHP; dans le récipé à l'amine à 41 °F, le MLP fournit des conversions moindres.

Zusammenfassung

In der Dextrosefreien Vorschrift bei 41 °F. für die Copolymerisation von Butadien und Styrol, die 6×10^{-4} Mol Initiator pro hundert Gramm Monomer verwendet, ergaben Methyloleat-Peroxyd (MOP) und Methyllinoleat-Peroxyd (MLP) höhere Polymerisationsgeschwindigkeiten und Umsätze als Cumolhydroperoxyd (CHP), und sie ergaben ebenso hohe Umsatzgeschwindigkeiten wie *p*-Menthan-Hydroperoxyd (PMHP). In der Peroxyd-Dextrose-Vorschrift bei 122 °F. wurde sowohl bei niedrigem wie bei hohem Dextroseniveau nur ungefähr ein halb mal soviel MOP (1.5×10^{-4} Mol) als CHP oder PMHP auf einer molaren Grundlage verwendet, um gleiche Umsatz- und Polymerisationsgeschwindigkeiten zu erhalten. In der Redoxvorschrift mit niedriger Dextrose bei 41 °F., die 6×10^{-4} Mol Initiator pro hundert Gramm Monomer benutzt, ergab MLP etwas höhere Umsätze als CHP oder PMHP, aber in der Aminvorschrift bei 41 °F. ergab MLP niedrigere Umsätze.